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(54) **FCC processing using catalyst compositions containing metal ion-exchanged zeolites.**

(57) A zeolite composition comprising a zeolite Y incorporated within a matrix, which zeolite contains ions of a metal selected from zinc, copper, cobalt, gallium, germanium, indium, tin, antimony and iron, and especially zinc, when used as a catalyst in hydrocarbon cracking, especially FCC, exhibits simultaneously activity enhancement, enhanced aromatic and branched chain paraffins in the gasoline fraction and passivation of both nickel and vanadium.

The catalyst composition can be prepared by incorporating the zeolite Y in a matrix material to provide a zeolite composition and thereafter subjecting the composition to metal ion-exchange.

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This invention relates to FCC processing using catalyst compositions containing metal ion-exchanged zeolites. In particular, the invention relates to FCC processes using a catalyst composition containing a zeolite into which a metal, especially zinc, ion has been incorporated by ion-exchange, which composition has improved catalytic properties.

5 Catalysts containing crystalline zeolites dispersed in an inorganic oxide matrix have been widely utilized in the production of gasoline by cracking of petroleum-derived feedstocks, particularly gas oil, using FCC technology.

Typically, in FCC, wide-pore zeolites having a faujasitic structure (X or Y zeolites) have been employed and, in particular, zeolite Y has proved especially popular commercially. Much work has been carried out in an attempt to further improve this catalyst, and such improvements have been achieved by including in the catalyst composition other additional zeolites, including medium-pore zeolites of the ZSM-5 family or by modification of the zeolite, including ionexchange treatment.

Such improvements include increased conversion, increased aromaticity of the gasoline, increased branching of the paraffins in the gasoline and improved passivation of certain metal contaminants present in the petroleum feedstock, especially vanadium and nickel which produce undesirable changes in the activity and selectivity of the contaminated catalyst. However, to date there has been no disclosure of the use of a catalyst composition so as to achieve all of these advantages at one and the same time.

Thus, US-A-4363720 and US-A-4500645 disclose the incorporation, separately into a zeolite catalyst composition, of a zinc treatment agent, especially zinc oxide. The zinc oxide is introduced into the composition by treating the zeolite with a zinc nitrate solution, subsequent processing of the catalyst composition resulting in precipitation of zinc oxide. According to US-A-4363720, this results in passivation of contaminant metals, especially nickel, while according to US-A-4500645, a reduction in the amount of gaseous component is achieved even when maintaining a high conversion so as to produce selectively a middle fraction.

US-A-3835030 is directed mainly to achieving improved activity of a zeolite by increasing its silica/alumina ratio. However, an additional improvement in activity is achieved by ion-exchanging the zeolite with a metal, such as a zinc, cation.

Where a gasoline having a high octane rating is required it is known to use, as an FCC catalyst, a matrix containing zeolite  $\beta$  instead of zeolite Y. According to EP-A-0258726, if the zeolite  $\beta$  has, ion exchanged onto it, Ga and/or Zn, then the resulting gasoline, in addition to high octane rating, also has a high aromaticity. The catalyst is prepared by heating the zeolite  $\beta$  in a solution of a salt of the metal, mixing the ion-exchanged zeolite  $\beta$  with the silica sol, oven drying, screening and then calcining. This will cause formation of the Ga and/or Zn oxide.

GB-A-1393501 describes zeolite (especially zeolite Y) catalysts ion exchanged with rare earth metal and zinc ions in controlled relative proportions so as to achieve improved thermal and steam stability properties. The ion exchange of the rare earth metal and/or zinc can be carried out prior or subsequently to incorporation of the zeolite in a matrix, especially kaolin.

EP-A-0073874 is directed to vanadium passivation in FCC and RCC catalysts and describes three tests for determining the likely effectiveness of metal additives in the catalyst, namely a lump formation, vanadia diffusion-compound formation and spectroscopic and thermal analyses. In particular,  $\text{TiO}_2$  and  $\text{MnO}_2$  scored highly, while ZnO gave poor results.

Surprisingly, we have found that a zeolite catalyst composition comprising a zeolite Y incorporated within a matrix, which zeolite Y contains certain metal, especially zinc, ions, as later described, when used as a catalyst in hydrocarbon cracking, especially FCC, exhibits simultaneously each of the following phenomena,

- i) activity enhancement, as compared with a composition in which the zeolite has not been metal ion exchanged,
- ii) enhanced aromatization of the gasoline fraction,
- (iii) enhanced branching of paraffins of the gasoline fraction,
- (iv) vanadium passivation of the catalyst and
- (v) nickel passivation of the catalyst.

Hereinafter, such a zeolite composition is referred to as "a metal ion exchanged zeolite catalyst composition".

Aspects of the present invention include

- 1) a method of cracking a vanadium and/or nickel containing hydrocarbon feedstock, which method comprises contacting the feedstock with the metal ion exchanged zeolite catalyst composition,
- 2) use of the metal ion exchanged zeolite catalyst composition in the passivation of vanadium and/or nickel during the cracking of a hydrocarbon feedstock, and
- 3) a method of cracking a hydrocarbon feedstock containing nickel and vanadium with a zeolite catalyst composition and, during the said cracking, simultaneously achieving enhanced activity of the zeolite

composition, enhanced branching of paraffins and aromatization of the gasoline fraction and passivation of both the nickel and vanadium, which method comprises a step, prior to cracking the hydrocarbon feedstock, of subjecting the zeolite of the zeolite catalyst composition to ion exchange with a metal.

Commercially acceptable results may be achieved even for feedstocks containing 2 ppm or even more of contaminant vanadium and/or nickel, or even 2 ppm of either vanadium or nickel or both. The catalyst may remain highly effective even if loaded with up to 100 ppm, possibly even up to 10,000 ppm by weight of the catalyst composition of vanadium and/or up to 100 ppm, possibly even up to 3000 ppm nickel.

As compared with an equivalent catalyst composition containing zeolite Y as control, a catalyst composition containing zeolite Y ion exchanged with a metal, especially zinc, ion may show an improvement in % conversion of at least 1%, possibly up to 11% or even 15%.

Likewise, a catalyst composition containing metal ion-exchanged zeolite Y may give an increase in hydrogen transfer during the cracking process so as to yield, by comparison with the control a 0.5-5% increase in aromatic content coupled with a 1-10% increase in branched chain paraffin content.

The metal ion exchanged zeolite catalyst composition is especially effective in simultaneously achieving the above phenomena (i)-(v) if it is obtained by preparing a composition comprising a protonated, for example an ammonium ion exchanged, crystalline zeolite Y and a matrix material and thereafter subjecting the resultant composition to ion-exchange to provide, on the composition, ions of the metal.

The metal may be any of zinc, copper, chromium, manganese, cobalt, gallium, germanium, indium, tin, antimony and iron. Zinc is especially preferred.

The amount of the metal, especially zinc, by weight of the total catalyst composition is preferably 0.1-3, especially 0.5-2, more especially 0.012 moles of the metal per 100g total catalyst composition.

For zinc, expressed as metallic zinc, the amount, by weight of the total composition, is preferably 0.05-2%, especially 0.1-1%, more especially 0.8%. When expressed as ZnO, a typical range of amounts is 0.02-2%.

The crystalline zeolite Y component of a composition used in the method of the present invention is usually present in the range from about 5% to about 50%, especially about 20% to about 40%, by weight of the total composition. The zeolite Y, in addition to modification by ion exchange with the above metal ions, may be modified in other ways, for example, by ionexchange with other ions, especially rare earth metal ions, by impregnation, or by hydrothermal or chemical treatments, especially such treatments which render the zeolite Y more siliceous.

Zeolitic additives can also be incorporated in the matrix prior or subsequent to metal ion exchange in preparing zeolite compositions used in the methods of this invention and such additives can be natural or synthetic in origin. Naturally occurring zeolites include gmelinite, chabazite, dachiardite, clinoptilolite, faujasite, heulandite, analcite, levynite, erionite, sodalite, cancrinite, mepherine, lazurite, scolecite, natrolite, offretite, mesolite, mordenite, brewsterite and ferrierite. Suitable synthetic zeolites are A,B,E,F,H,J,L,Q,T,W,X,Y,Z, N-A, alpha, beta, omega, rho, the EU types, the FU types, the Nu types, the ZK types, the ZSM types, the  $\text{AlPO}_4$  types, the SAPO types, the pentasil types, the LZ series and other similar materials.

In a preferred embodiment of the invention, the preparation of the zeolitic composition includes the step of converting the zeolite Y to a form which is most applicable for the catalytic cracking method prior to the metal ion exchange. In general this involves a sequence of preliminary ion-exchange and calcination treatments to introduce acid groups into the zeolite Y, stabilise the structure, and remove alkali metal cations. The preferred method of achieving this end, well known in the art, is to exchange the zeolite with solutions containing ammonium ions and/or rare earth ions (either a pure rare earth compound or a mixture).

Such treatment can be carried out either on the zeolite before or after its incorporation into the matrix, and can be carried out on a filter press, filter table, or filter belt, or by slurring the zeolite/catalyst in a tank.

It should be mentioned that although, as mentioned above, preparation of the zeolite Y itself might involve calcination, such a treatment should not be carried out subsequent to the metal ion-exchange step. In any event, in a preferred process of preparing a catalyst composition for use in accordance with the invention, such a calcination step is not included.

An especially preferred zeolite is a zeolite Y, which before the metal ion-exchange is in the  $\text{NH}_4$ -Y or H-Y form.

The matrix into which the zeolite Y is incorporated can be selected from a wide range of components. Suitable components include: naturally occurring or synthetic clays, including kaolin, halloysite and montmorillonite; inorganic oxide gels such as silica gel, and including binary gels such as silica-alumina, silica-zirconia and silica-magnesia, aluminium phosphates, ternary combinations such as silica-magnesia-alumina; and crystalline inorganic oxides such as silica, alumina, titania and zirconia.

An especially preferred matrix comprises an inorganic oxide gel, such as a silica sol and alumina, for example, a crystalline alumina.

A typical catalyst composition prior to the metal ion exchange step comprises, by weight of the total weight

of the composition,

	zeolite - HY - 20-40, preferably 25-35, especially 30%				
5	inorganic oxide gel - 10-30, " 20-30, " 25%				
	alumina - 3-15, " 5-15, " 10%				
10	clay - 30-50, " 30-40, " 35%				

The metal ion exchange step may be carried out by treating the composition with an aqueous solution of the metal salt at a temperature of from ambient, for example 25°C, up to about 100°C, preferably (at least for zinc) at least 60°C, more preferably at least 70°C, especially 80°C. The resultant product may be filtered, washed and dried, preferably at a temperature just above boiling, for example, at 105°C.

We find, surprisingly, that a catalyst composition comprising zeolite Y containing metal ions, especially when the ion exchanged zeolite is prepared by the method described above, and more especially such a catalyst composition ion-exchanged with zinc, may be used to provide, at one at the same time, (i) activity enhancement, (ii) increased aromaticity and branched chain paraffin content of the gasoline and (iii) improved passivation of both vanadium and nickel.

The invention will now be described in more detail with reference to the following Examples.

In the Examples, the following definitions apply.

#### 25 Definitions

Kinetic Conversion	$= \frac{\text{Wt. \% Conversion}}{100 - \text{wt. \% Conversion}}$
Kinetic H <sub>2</sub>	$= \text{Wt. M H}_2\text{O-overKinetic Conversion}$
30 Specific Coke	$= \frac{\text{Wt. \% Coke} - 0.3}{\text{Kinetic Conversion}}$

#### Example 1 - Preparation of Zinc Containing Catalyst

35 The following composition was slurried into 3000 mls of deionized water, namely 300g zeolite HY, 250g silica sol binder, 100g pseudo-boehmite alumina and 350g clay. The slurry was spray-dried, washed and subjected to ammonium ion-exchange in the usual manner. The ammonium exchanged composition was filtered, washed and oven-dried. The resultant composition (100 gms) was slurried in 300 ml deionized water at 80°C. To the slurry catalyst was added 4.9g of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O dissolved in 20 ml deionized water. The mixture was stirred at 80°C for a further ten minutes, then filtered, washed and dried at 105°C for sixteen hours.

40 The parent catalyst was labelled as Catalyst A and the zincexchanged catalyst as Catalyst B. Catalyst B was analysed for zinc and contained 1% ZnO.

#### Example 2 - Microactivity Test (MAT) of Catalysts A and B

45 Prior to MAT evaluation, both catalysts A and B were hydrothermally deactivated in 100% steam at 816°C for 5 hours. MAT test conditions employed were as follows:

50	Feed type	-	Kuwait waxy distillate
	Temperature	-	960°F
	Weight Hourly Space	-	13.5
55	Velocity (WHSV)		

Th MAT data of major yields for catalysts A and B is given in Table 1 below.

Table 1MAT Data

	Catalyst A	Catalyst B
-----		
Conversion (wt.%)	67	76
Gasoline (wt.%)	46.3	51.7
LCO (wt.%)	22.8	18.8
HCO (wt.%)	10.4	5.6
LPG (wt.%)	16.1	17.2
Dry Gas (wt.%)	1.9	2.4
Specific Coke	1.13	1.28
Kinetic H <sub>2</sub>	0.048	0.075

The fact that wt.% conversion by Catalyst B after severe steam deactivation is 9 units higher than that of Catalyst A (Table 1) is a clear indication that zinc has enhanced the activity of the catalyst significantly (though this enhanced activity is accompanied by a high level of H<sub>2</sub>).

It might have been considered that such enhanced activity was associated (as in rare earth containing catalysts) merely with stability enhancement by the zinc of the zeolite structure. In order to determine whether or not this was the case both the fresh and steam deactivated catalyst samples for both catalysts A and B were subjected to surface area and crystallinity measurements. It was found that surface area retention and crystallinity for both catalysts A and B were similar (both about 67% for catalyst A and both about 68% for catalyst B). This shows clearly that zinc does not stabilize the zeolite structure and indicates that enhancement of activity is by a different mechanism.

From a partial analysis of the gasoline produced by catalysts A and B in the MAT unit it appeared the gasoline composition contained significantly increased amounts of both aromatic and branched chain paraffin compounds.

Example 3 - Nickel Passivation

Catalysts A and B were impregnated with 1000 ppm of Ni. The Ni impregnated catalysts were steam deactivated at 816°C for 5 hours and their catalytic performance was evaluated by MAT.

The MAT data of major yields for the Ni impregnated catalysts is given in Table 3 below.

Table 3MAT Data for Ni Impregnated Catalysts

	Catalyst A	Catalyst B
-----		
Conversion (wt.%)	67	75
Gasoline (wt.%)	45.6	49.0
LCO (wt.%)	21.1	18.2
HCO (wt.%)	10.7	6.3
LPG (wt.%)	16.7	18.9
Dry Gas (wt.%)	2.1	2.8
Specific Coke	1.20	1.41
Kinetic H <sub>2</sub>	0.095	0.11

Nickel is a well known dehydrogenating catalyst. Thus, the degree of the increase of H<sub>2</sub> yield in the presence of nickel can be used to assess the nickel tolerance of FCC catalysts. To this end, the kinetic H<sub>2</sub> of catalysts A and B in the presence and absence of nickel is compared in Table 4 below.

Table 4Comparison of Ni Tolerance for Catalysts A and B

	<u>Kinetic Hydrogen</u>		
	0 ppm Ni	1000 ppm Ni	% Increase
-----			
Catalyst A	0.048	0.095	98
Catalyst B	0.075	0.11	46

Example 4 - Vanadium Passivation

Catalysts A and B were impregnated with 3000 ppm of V. The V impregnated catalysts were steam deactivated at 788°C for 5 hours and their vanadium tolerance assessed by MAT, and the data of major yields for the V impregnated catalysts is given in Table 5 below.

Table 5MAT Data for V Impregnated Catalysts

	Catalyst A	Catalyst B
-----		
Conversion (wt.%)	66	77
Gasoline (wt.%)	44.0	49.5
LCO (wt.%)	22.2	17.6
HCO (wt.%)	11.5	5.9
LPG (wt.%)	15.8	18.5
Dry Gas (wt.%)	2.5	3.2
Specific Coke	1.83	1.66
Kinetic H <sub>2</sub>	0.19	0.12

Vanadium selectively attacks the zeolite structure and this leads to loss in catalytic activity and an increase in H<sub>2</sub> and coke yields.

The activity of catalyst B in the presence of V is 11 units higher than that of catalyst A. Moreover, the specific coke and kinetic H<sub>2</sub> for catalyst B is lower than that of catalyst A. This clearly demonstrates the vanadium passivating property of zinc.

From the above Examples, it can be seen that a method embodying the invention for cracking a hydrocarbon feedstock using a metal ion exchanged zeolite Y catalyst composition provides, at one and the same time, increased conversion, and increased aromatic and branched chain paraffin content of the gasoline so that enhanced motor octane is to be expected. Furthermore, the composition is also, at the same time, highly effective in passivating both nickel and vanadium.

**Claims**

1. A method of cracking a vanadium and/or nickel containing hydrocarbon feedstock, which method comprises contacting the feedstock with a zeolite catalyst composition comprising a zeolite Y incorporated within a matrix, the zeolite Y containing metal ions selected from zinc, copper, cobalt, gallium, germanium, indium, tin, antimony and iron.
2. A method of cracking a hydrocarbon feedstock containing nickel and vanadium with a zeolite catalyst composition containing zeolite Y and, during the said cracking, simultaneously achieving enhanced activity of the zeolite composition, enhanced branching of paraffins and aromatization of the gasoline fraction and passivation of both the nickel and vanadium, which method comprises a step, prior to cracking the hydrocarbon feedstock, of subjecting at least the zeolite Y of the zeolite catalyst composition to ion exchange with a metal selected from zinc, copper, cobalt, gallium, germanium, indium, tin, antimony and iron, so as to provide metal ions on the zeolite Y and utilising the said metal ion containing zeolite Y in the said cracking of the hydrocarbon feedstock.
3. A method according to claim 1 or claim 2, wherein the feedstock contains at least 2 ppm of vanadium and/or nickel.
4. A method according to claim 3, wherein the feedstock contains at least 2 ppm of vanadium.

5. A method according to claim 3, wherein the feedstock contains at least 2 ppm of nickel.
6. A method according to any preceding claim, wherein during the said cracking, the catalyst composition becomes loaded with at least 100 ppm by weight of the catalyst composition of vanadium.
7. A method according to claim 6, wherein the catalyst composition becomes loaded with up to 10,000 ppm of vanadium.
8. A method according to any preceding claim, wherein during the said cracking, the catalyst composition becomes loaded with at least 100 ppm by weight of the catalyst composition of nickel.
9. A method according to claim 8, wherein the catalyst composition becomes loaded with up to 3000 ppm of nickel.
10. A method according to any preceding claim in which the zeolite catalyst composition has been prepared by incorporating the zeolite Y in a matrix and thereafter subjecting the zeolite Y containing matrix to ion exchange with the metal ion.
11. A method according to claim 10, wherein the zeolite catalyst composition has been prepared by a method comprising the steps of
  - (a) incorporating the zeolite Y in a matrix material to provide a zeolite composition,
  - (b) prior to, simultaneously with or subsequently to step (a), subjecting the zeolite Y to ammonium ion exchange, and
  - (c) after steps (a) and (b) subjecting the zeolite composition to metal ion-exchange to provide the metal ions on the zeolite Y.
12. A method according to any preceding claim, wherein the metal ions are present in an amount, expressed as the lowest metal oxide, of from 0.1 to 3% by weight of the total weight of the catalyst composition.
13. A method according to any preceding claim, wherein the metal ions are selected from zinc and copper.
14. A method according to claim 13, wherein the metal ions are zinc.
15. A method according to any preceding claim, wherein the matrix comprises at least one of a silica sol and alumina.
16. A method according to claim 15, wherein the matrix comprises a silica sol and alumina.
17. A method according to claim 11, wherein subsequent to the said incorporation step (a) but prior to the said metal ion-exchange step (c), the zeolite Y is subjected to the ammonium ion exchange step (b).
18. A method according to any preceding claim, wherein the metal ions have been introduced into the zeolite catalyst composition by heating a slurry of the composition in a solution of a salt of the metal at a temperature of from ambient temperature to 100°C inclusive.
19. A method according to claim 18, wherein the metal salt is zinc nitrate.
20. A method according to any preceding claim, which includes the preliminary step of subjecting the zeolite catalyst composition to hydrothermal deactivation.
21. Use of a zeolite catalyst composition in the passivation of vanadium and/or nickel during the cracking of a hydrocarbon feedstock, which zeolite catalyst composition comprises a zeolite Y incorporated within a matrix, the zeolite containing metal ions selected from zinc, copper, cobalt, gallium, germanium, indium, tin, antimony and iron.
22. Use according to claim 21 for the simultaneous passivation of vanadium and nickel.
23. Use according to claim 21 or claim 22, wherein the feedstock contains at least 2 ppm of said contaminant

metal.

24. Use according to claim 23, wherein the feedstock contains at least 2 ppm of vanadium.
- 5 25. Use according to claim 23, wherein the feedstock contains at least 2 ppm of nickel.
26. Use according to any one of claims 21 to 25, wherein during the said cracking, the catalyst composition becomes loaded with at least 100 ppm by weight of the catalyst composition of vanadium.
- 10 27. Use according to claim 26, wherein the catalyst composition becomes loaded with up to 10,000 ppm of vanadium.
28. Use according to any one of claims 21 to 27, wherein during the said cracking, the catalyst composition becomes loaded with at least 100 ppm by weight of the catalyst composition of nickel.
- 15 29. Use according to claim 28, wherein the catalyst composition becomes loaded with up to 3000 ppm of nickel.
30. Use according to any one of claims 21 or 22, in which the zeolite catalyst composition has been prepared by incorporating a zeolite Y in a matrix and thereafter subjecting the zeolite Y containing matrix to ion exchange with the metal ions.
- 20 31. Use according to claim 30, wherein the zeolite catalyst composition has been prepared by a method comprising the steps of
  - (a) incorporating the zeolite Y in a matrix material to provide a zeolite composition,
  - 25 (b) prior to, simultaneously with or subsequently to step (a), subjecting the zeolite Y to ammonium ion exchange, and
  - (c) after steps (a) and (b) subjecting the zeolite composition to metal ion-exchange to provide the metal ions on the zeolite Y.
- 30 32. Use according to any one of claims 21 to 31, wherein the metal ions are present in an amount expressed as the lowest metal oxide, of from 0.1 to 3% by weight of the total weight of the zeolite catalyst composition.
33. Use according to any one of claims 21 to 32, wherein the metal ion is selected from zinc and copper.
- 35 34. Use according to claim 33, wherein the metal ion is zinc.
35. Use according to any one of claims 21 to 34, wherein the matrix comprises at least one of a silica sol and alumina.
- 40 36. Use according to claim 35, wherein the matrix comprises a silica sol and alumina.
37. Use according to claim 31, wherein subsequent to the said incorporation step (a) but prior to the said metal ion-exchange step (c), the zeolite Y is subjected to the ammonium ion exchange step (b).
- 45 38. Use according to any one of claims 21 to 37, wherein the metal ions have been introduced into the zeolite catalyst composition by heating a slurry of the composition in a solution of a salt of the metal at a temperature of from ambient temperature to 100°C inclusive.
39. Use according to claim 38, wherein the metal salt is zinc nitrate.
- 50 40. Use according to any one of claims 21 to 39, which includes the preliminary step of subjecting the zeolite catalyst composition to hydrothermal deactivation.
41. Use, for simultaneously increasing the aromatic and branched chain content in a gasoline produced by a hydrocarbon cracking process using a zeolite Y composition, of a said zeolite Y containing metal ions selected from zinc, copper, cobalt, gallium, germanium, indium, tin, antimony and iron.
- 55